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<p>To aid in the development of boron-enhanced fluoronitramino explosives, the kinetics of individual reactions are measured over wide temperature ranges. The following rate expressions, in cm³molecule⁻¹s⁻¹, were obtained. For BO₂ + H₂ → HOBO + H k(500-1250 K) = 3.6x10⁻¹¹exp(-4198 K/T), for BO + CO₂ → BO₂ + CO k(780-1200 K) < 2.7x10⁻¹⁴, for BO₂ + CO → BO + CO₂ k(1000 K) < 6.0x10⁻¹⁴, for BO + O₂ → BO₂ + O k(300-960 K) = 7.9x10⁻¹²exp(161 K/T).</p>					
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PROGRESS

Introduction

Our goals are:

- (1) to make accurate measurements, over wide temperature ranges, of rate coefficients for boron combustion in C/H/N/O/F environments, of importance to the development of new underwater explosives, and
- (2) to use the measurements to obtain a further understanding, to allow predictions for additional reactions occurring with such explosives.

Reactions for study are selected on the basis of modeling studies.¹⁻⁴ The results, in turn, allow improvement of the models. In the past year measurements have been made on



A High-Temperature Fast-Flow Reactor (HTFFR) was used to measure rate coefficients for reaction 1 and upper limits for 2a and 2b. The High-Temperature Photochemistry (HTP) technique was used to obtain an upper limit for 2a, as well as to measure rate coefficients for reaction 3.

Experimental

The HTFFR and HTP reactors and procedures have been described frequently.⁵ The reactions were studied in Ar bath gas under pseudo first-order conditions with BO or BO₂ as the minor reactant. For BO production in the HTFFR studies, a mixture of B and N atoms was produced by passing a trace of diborane, B₂H₆, mixed with N₂ in Ar bath gas through a microwave discharge. NO was added downstream to produce O atoms, via $\text{N} + \text{NO} \rightarrow \text{N}_2 + \text{O}$, which resulted in BO formation, Fig. 1. BO₂ was produced by reacting BCl₃ with the products resulting from passing a CO₂/Ar mixture through a microwave discharge, Fig. 2. For the HTP studies, BO radicals were produced by multi-photon dissociation of BCl₂(OCH₃).⁶

The relative [BO] was monitored via laser-induced fluorescence of the $A^2\Pi-X^2\Sigma$ (1,1) transition at 436 nm, pumped at 403.55 nm on the (1,0) transition.⁷ Relative [BO₂] was monitored by pumping the $B^2\Sigma-X^2\Pi$ (000-000) transition at 406.7 nm and observing the $A^2\Pi-X^2\Pi$ (002-000) transition at 435.8 nm.⁸

Results

BO₂ + H₂

Rate coefficient measurements were made from 500 - 1250 K, at total pressures from 4.1 - 9.3 mbar, corresponding to total concentrations of 3.0×10^{16} to 6.7×10^{16} .

molecules cm⁻³, average gas velocities from 21 to 106 m s⁻¹, and reaction zone lengths selected at 10 or 20 cm. The data were fitted to a $k(T) = A \exp(-E/T)$ expression, by weighted linear regression,⁹ to yield

$$k_I(500-1250 \text{ K}) = 3.6 \times 10^{-11} \exp(-4198 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (4)$$

This result is compared in Fig. 3 to the expression $k_I(T) = 3.0 \times 10^{-12} \exp(-1475 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ estimated by Brown *et. al.*,¹⁻³ which may be seen to differ significantly. The primary temperature range of interest for boron combustion is 1800 - 3000 K.¹⁻⁴ Extrapolation of eq. 4 to these temperatures would result in rate coefficients approximately 3 - 5 times greater than used in these models.

BO + CO₂

This reaction was studied between 780 to 1200 K in an HTFFR, and yielded the upper limit

$$k_{2a}(780 - 1200 \text{ K}) < 2.7 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (5)$$

Measurements by the HTP technique mirrored this result:

$$k_{2a}(300 - 870 \text{ K}) < 9.6 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (6)$$

The Brown *et. al.* model uses $k_{2a} = 1.8 \times 10^{-11} T^{0.37} \exp(-7900 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which at 1200 K is more than an order of magnitude larger than the upper limit of eq. 6 and would indicate a fast reaction in the 1800 - 3000 K range.

The reverse reaction, 2b, was studied at 1000 K and gave an upper limit

$$k_{2b}(1000 \text{ K}) < 6.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (7)$$

Based on the Gibbs free energy of reaction 2a, -14.6 kJ mol⁻¹ at 1000 K, and its experimental upper limit (eq. 5), the upper limit at 1000 K for reaction 2b is calculated to be $4.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, consistent with eq. 7. To help understand why reactions 2a and b are so slow we plan to make *ab initio* calculations to find transition states and associated activation barriers.

BO + O₂

This reaction was studied over the 300 to 960 K temperature range at pressures from 67 to 271 mbar (9.7×10^{17} to 6.5×10^{18} molecules cm⁻³). At temperatures of 300, 500, and 950 K the reaction was found to be pressure independent. The results may be seen to be in agreement with the study by Stanton *et. al.*,⁶ Fig. 4; those authors had limited the pressure dependence study to room temperature. The combined data sets were fitted as above to yield

$$k_3(300 - 960 \text{ K}) = 7.9 \times 10^{-12} \exp(161 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \quad (8)$$



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Gentlemen:

Enclosed please find the contractually required 2 copies of the annual report on the referenced grant.

Sincerely,

Arthur Fontijn
Professor & Head of the Department

AF:jm
Enc.

PLANS

Reactions to be studied will be selected on the basis of the ongoing Aerodyne-Princeton modeling work.¹⁻³ These include the reactions of BO with N₂O, HCl, and HF, and of BF with BF₃, O₂, and H₂O.

As already mentioned, we plan ab initio studies in an attempt to explain the low reactivity of reaction (2).

In last year's progress report, we reported on the BO + HCl reaction. There are three exothermic spin-allowed exit channels for this reaction: HBO + Cl₂, OBCl + H, and BCl + OH. By making use of an HTFFR mass-spectrometer facility, developed recently with other support,¹⁰ we plan to try to distinguish between these.

PARTICIPANTS AND CONTACTS

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PUBLICATIONS AND AWARDS

1. D.P. Belyung, G.T. Dalakos, Q. Zhang, J-D.R. Rocha, and A. Fontijn, "Wide-Temperature Range Studies of BO and BO₂ Reactions", Extended Abstract for presentation at the Eastern States Section of the Combustion Institute meeting, December 9-11, 1996.
2. G.T. Dalakos, "BO Reactions Over A Wide Temperature Range", M.Sc. Thesis, Rensselaer Polytechnic Institute, Troy, NY, May 1996.

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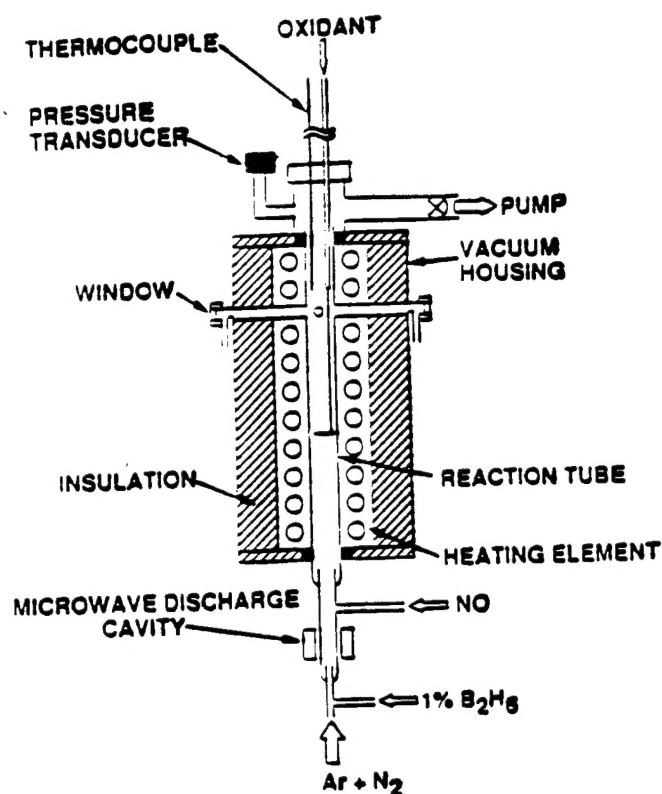


Figure 1. Schematic of the HTFFR BO production method

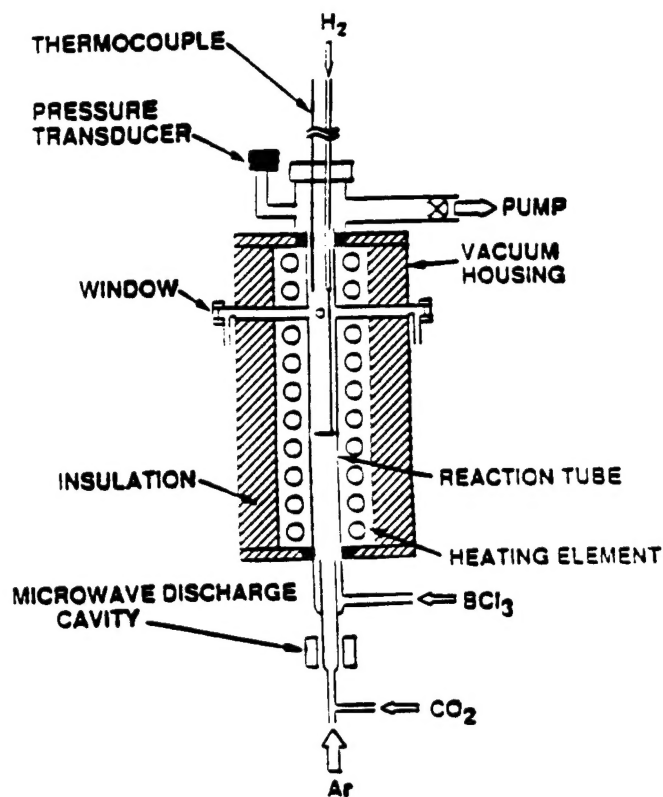


Figure 2. Schematic of the HTFFR BO₂ production method

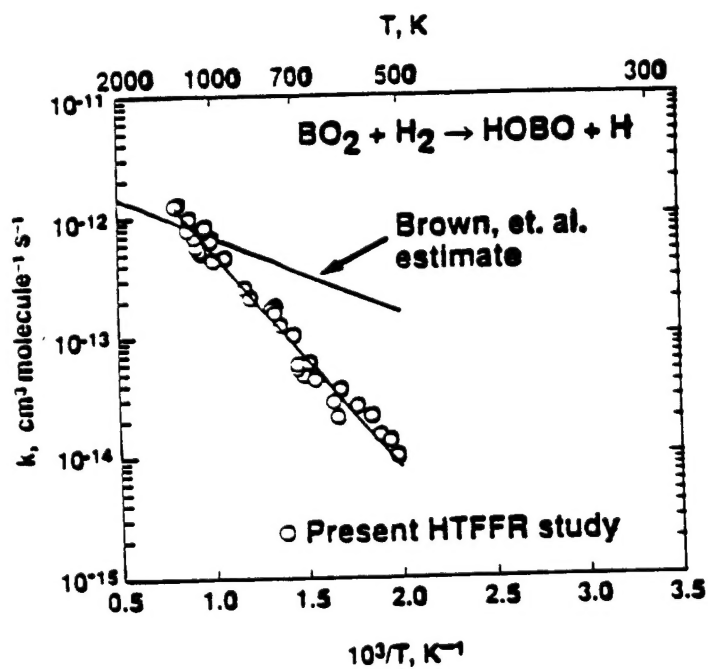


Figure 3. Summary of the BO₂ + H₂ rate coefficients

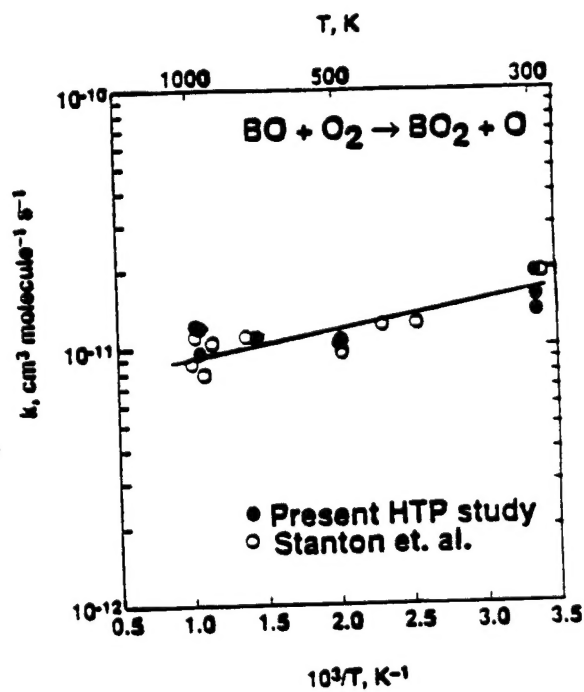


Figure 4. Summary of the BO + O₂ rate coefficients